PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) HIGH CAPACITY METAL/AIR BATTERY

(71) We, LEESONA CORPORATION, a Corporation organised and existing under the laws of the State of Massachusetts, United States of America, of 333 Strawberry Field Road, Warwick, Rhode Island, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to air or oxygen-depolarized cells for the electrochemical generation of electrical current. More particularly, the invention is directed to the improved construction of such an air or oxygen-depolarized cell as is described in British Patent Specification Nos. 1,138,468, 1,133,469, 1,176,486 and 1,176,487—9.

Air or oxygen depolarized cells of the type where only the anode of the cell is chemically changed or consumed during operation are known in the prior art. The first cells of this type while being suitable for application where only slow discharge was required were not practical where rapid discharge was necessary. The cathodes of such cells were carbon structures making recharging impractical if not impossible.

More recently, however, the metal/air or metal/oxygen systems as described in the aforesaid British Patent Specifications Nos. 1,138,468 and 1,138,469 have become increasingly attractive particularly from the standpoint of obtaining a high energy to density and high energy to volume ratio and rapid discharge and recharge. The ability to obtain the aforesaid advantages is primarily a result of the highly efficient cathodes employed. It has been found, however, that it is difficult to operate a battery of cells capable of rapid discharge and high current drains at a constant voltage at low current densities. That is, at low current densities, the voltage of the battery will become unduly high. Furhermore, if the air depolarized cells are stacked close together so as to generate sufficient internal heat in the battery to permit operation at low temperatures at low current drains, the cells will polarize, overheat and not support the external loads at high current drains. Conversely, if the cells are spaced further apart to permit flow of greater amounts of air preventing polarization and overheating at high current drains, cell performance deteriorates at low temperatures.

The present invention is intended to eliminate or reduce these difficulties.

Accordingly the invention provides a metal/air battery comprising a plurality of cells each comprising a non-consumable air-depolarized cathode comprising a hydrophobic member and a conductive catalytic coating on one surface of said member, a consumable metal anode spaced from and opposite said catalytic coating on said cathode and an electrolyie in the space separating said cathode from said anode, spacers separating said plurality of cells from each other permitting air flow to said cathodes, and means constructed and arranged integral with said plurality of cells for propelling air across said air-depolarized cathodes.

These and other features of the inventron will be more readily apparent from the following detailed description of one embodiment given by way of example and with reference to the accompanying drawings.

In the drawings:—

Figure 1 is a perspective partially broken away view of a metal/air battery including a voltage regulator and blower;

Figure 2 is a perspective partially broken away view of a single metal/air bi-cell of the type utilized in the battery of Figure 1;

Figure 3 is a fragmentary front view partially broken away of an inter-cell spacer of the type utilized in the battery of Figure 1; and

Figure 4 is a simplified circuit of a preferred voltage regulator utilized in the battery shown in Figure 1 with an accom-

panying graph illustrating the function of the regulator.

The aforesaid objects of the present invention are obtained by utilizing a metal/air battery design whereby a plurality of metal/air bi-cells comprising a non-consumable envelope cathode comprising a hydrophobic membrane and a conductive catalytic coating on the inner surface of said membrane, a consumable replaceable metal anode position within the envelope cathode and an electrolyte between the anode and cathode, are stacked together in a receptacle. The bi-cells are separated from each other and from the end plates of the battery by intercell spacers to permit air flow to the air depolarized cathodes. The battery receptacle, to permit air flow, has a plurality of openings at both top and bottom. To facilitate the replacement of the replacable anodes in the plurality of cells, a pressure plate with a drive screw mechanism is positioned at one end of the battery of cells. Accordingly, the pressure on the cells can be applied and released with a minimum of effect. In the preferred embodiment of the invention, the cover portion covers the openings at the top of the battery receptacle and includes a housing for an air blower and voltage regulator. Alternatively, the top or cover portion will merely enclose the battery of cells and have electrical take-off means.

In operation of the battery, the voltage regulator will permit the battery to provide a current output over a fixed or constant voltage range regardless of how low or high the current output. More particularly, when the cell is to be operated at a constant voltage range, but over a wide current density range, the voltage regulator will cut selected cells of the battery into and out of operation to maintain a uniform voltage. As a result of a series connection between the blower and the voltage regulator, the blower will not be in operation when the selected cells are cut out, but will be in operation to enhance air movement within the battery when all of the cells are being utilized. Accordingly, the battery is capable of operating at virtually any current density output over a constant voltage range and, furthermore, will operate over the entire range of the battery's capacity at permissible internal battery temperatures at ambient conditions of from -40°F. to 150°F.

More specifically, referring primarily to Figures 1—3 of the drawing, the battery comprises a plurality of cell modules 10 comprising an envelope cathode made up of a bi-cell frame 11 and reactive cathodes 12 and 13. The frame contains cell guide supports 14 which facilitate the positioning of the cell module in the battery casing and moldings 15 which house positive leads 16 which are in electrical contract with the envelope cathode. In the embodiment shown, the cathode is made up of a continuous hydrophobic polymer membrane 17, a conductive support screen 18, and an electrocatalyst layer pressed into and around the support screen. The hydrophobic polymer membrane is polytetrafluorethylene and the electrocatalyst is a uniform mixture of platinum bonded with polytetrafluoroethylene particles. The catalyst and bonding agent are present at a weight ratio of 10 parts to 3 parts. Anode 20 comprising top portion 21 and a metal body 26 fits into the envelope cathode and is locked into position by negative terminals 23 which fit into negative terminal sockets 24. The terminals are in electrical contact with the anode body through the anode top. Negative leads 25 emerge from the terminal sockets at each side of the cell. The aforesaid, together with the mirror cathode contacts 16, provide a wiring system for the battery. This system virtually eliminates any possibility of the battery becoming faulty because of loose or broken electrical connections. In the embodiment shown, the anode comprises a porous zinc body 26 pressed around a conductive screen 27. Anode separator paper 28 completely surrounds the anode and serves as a matrix for retaining the cell electrolyte which is, in this instance, a solution of aqueous 31 percent potassium hydroxide.

The battery 40 is made up as a plurality of the cell modules 10, shown in Figure 2, separated from each other by means of inter-cell spacers 30, shown in Figure 3, but not visible in Figure 1, positioned in casing 41. The casing has openings 42 at the top and bottom. A fixed end plate, not shown, it at one end of the battery and a movable end plate 43 is positioned at the other end of the battery. The inter-cell spacers 30 which are adjacent to the end plates and between each two cell modules must be air permeable, permitting air flow to the reactive cathodes. The inter-cell spacer illustrated in Figure 3 comprises a plurality of plastic mesh layers laminated together to provide a dense, air permeable body. Drive screw mechanism 46 permits rapid application and release of pressure to facilitate the removal of the anodes 20 from the envelope cathodes. The cover portion of the battery 43 comprises housings 43a and 43b for blower 44 and voltage regulator 45. A handle 46 is attached to housings 43a and 43b for carrying the battery. The plurality of cell modules are electrically connected in series by interconnecting negative leads 25 and positive leads 16. The electrical leads are then taken to, and through the top of the battery and

connected to the voltage regulator 45. The voltage regulator is connected in series with the blower 44. The battery is connected to a load by means of terminal 47. Cover 43 is retained on casing 41 by clamps 48.

Figure 4 is a simplified illustration of the electrical circuitry of the battery which for purposes of the present discussion is broken down into a primary and auxiliary source. Referring to Figure 4, primary source 40a is connected to operate a variable load RL such as a trans-receiver radio device which draws high current in its transmitting condition and low current in its receiving condition. Graph 50 typifies the undesirable voltage fluctuation of the battery under such high-low load current conditions by means of a curve 51. If it is assumed that the high current load condition causes a drop of substantially three volts (shown as e in the graph) in the primary source 40a, then an auxiliary source 40b supplying three volts in a no-load condition may be connected in series with source 40a to provide high voltage at terminal 52. Relay 53 by way of switch contact 54 serves to connect the auxiliary current source 40b to the load at terminal 55 whenever a drop of voltage e is sensed as a result, for example, of switching from receive mode of operation at the load RL where the load voltage would be e to a transmit mode of operation where the load voltage received from only the primary source 40a drop to a value E—e.

Suitable means may be used for detecting either a change in load current or a change in voltage such as, for example, a sensing resistor 56 of low resistance coupled in the load current path to signify a voltage change to a biased amplifier 57. The amplifier is in essence a switch which operates relay 53 to close contacts 54 when a voltage sensed by resistor 56 overcomes a cut-off bias of the amplifier 57 at some predetermined threshold value dependent upon the operating parameters of the particular battery load combination which is to be regulated. In order to assure that there is no loss of power to the load RL at any instance as the auxiliary source 40b is switched in or out of circuit, uni-directional means such as a solid state rectifier 58 couples the primary source 40a continuously to the load RL. However, the auxiliary source 40b is connected directly to load RL by contact 54 only when the load current exceeds the predetermined threshold value. Because of the polarity of rectifier 58, the auxiliary source 40b will pass current only through the load RL when switch 54 is closed. Furthermore, the potential of primary source 40a essentially cuts off conduction through rectifier 58 when switch 54 is closed. This gives a smooth transition between the two conditions without interruption of power. Similar isolation may alternatively be accomplished by other means such as a second relay.

While in the embodiment shown, a single transistor is utilized between two different load conditions, the principles can be used to produce a series of different voltage steps by using more than one auxiliary current source. Similarly, with certain types of load, a similar affect may be accomplished by coupling batteries or other current sources in parallel rather than in series. This is particularly effective when constant current sources are employed. Furthermore, although in the embodiment shown the end cells of the battery unit function as the auxiliary current source and are cut in and out, it can be desirable to utilize the middle cells of the unit for this purpose. The circuitry employed is not a part of the present invention and can be modified as long as select cells of the battery are switched in and out to regulate the voltage or current. Because of the simplicity of the design, however, the preferred circuitry is as shown in Figure 4, described fully in U.S. Patent Specification No. 3,474,324.

Blower 44 which is connected in series with the auxiliary power source 40b can be any small fan or the like capable of enhancing flow of air over the top of and between the cell modules and out through the bottom openings of the battery receptacle. It may be desirable to employ baffling means of the like, not shown, in the top of the cover portion of the battery to uniformly distribute the air to the plurality of cells of the battery. Since the blower is in series connection with the auxiliary power source 40b as shown in Figure 4, it will only be in operation when all of the cells of the battery are in use. By utilizing the blower of the aforesaid type, the spacing of the cells can be kept to a minimum permitting operation at low current densities at very low temperature since, under such conditions, most of the sensible heat of the battery is retained within the casing. Accordingly, the battery can be operated at permissible operating internal temperature over its full current density range at virtually any ambient temperature ranging from −40° to 150°F.

The aforesaid battery after initial discharge can be re-activated by replacing the spent anodes. The complete operation is conveniently accomplished as follows:

1. The battery cover is removed;

2. Pressure on the plurality of cells is released by turning pressure control knob 26 counter-clockwise;

3. The spent anodes which are now loose in the envelope cathodes are removed and discarded;

4. An anode having electrolyte impregnated in the anode separator is inserted into each envelope cathode;

5. Pressure control knob 26 is turned clockwise to reapply pressure on the cell, and

6. The battery cover is replaced.

The battery is now ready for operation. Inasmuch as the cathodes are air depolarized and non-consumable, it is not necessary to service the cathodes at all. The electrolyte is replenished at the same time the anodes are inserted since the anode separator assembly is impregnated with electrolyte. As apparent, since the envelope cathodes are not moved substantially relative to the adjacent cathodes, the electrical leads are not disturbed. The entire recharging operation is extremely simple and can be accomplished virtually anywhere without need of an external power source. Accordingly, the battery is imminently suitable for mobile field operations.

The various components of the metal/air or metal/oxygen battery are described fully in the aforesaid British Patent Specifications Nos. 1,138,468, 1,138,469. Briefly, however, the cathodes employed comprise a hydrophobic membrane which is in contact with a conductive metal support screen or mesh and a catalytic layer. The membrane which is to be used can be any material which is hydrophobic and permits the passage of gas, but precludes the flow of aqeous materials. Exemplary materials are the polymers of fluorinated hydrocarbons such as polytetrafluoroethylene, polytrifluoroethylene, polyvinylfluoride, polyvinylidenefluoride, and hydrophobic copolymers of the monomers of two or more of the above materials or co-polymers of such materials with acrylonitrile, methacrylate and polyethylene. The polymers normally will have a porosity of from 15 to 85 percent and a uniform pore size distribution of from 0.01 to 100 microns and a thickness of 0.5 to 10 mils. The catalyst used to coat the hydrophobic polymer are the pure elements, alloys, oxides, or mixtures thereof which are effective in promoting an electrochemical reaction. More specifically, operable materials include the elements, alloys, oxides, or mixtures of Group IB, IIB, IV, V, VI, VII, and VIII metals of the Mendelyeev's Periodic Table. The metal support screen can be any material which conducts an electrical current and will withstand the corrosive environment of the battery. Such materials include nickel, zirconium, titanium, and tungsten screens and expanded meshes. Moreover, it is possible to apply a hydrophilic polymer or other suitable hydrophilic material such as paper over the catalytic layer which will be in contact with the electrolyte of the battery when in operation.

The anodes which are to be used herein can be any conventional solid electroconductor employed in a metal/air or metal/oxygen cell such as metals, metaloids, alloys, and heavy metal salts. It is only essential that the material selected be chemically reactive with a compatible electrolyte and be more electro-positive than oxygen. Such materials include lead, zinc, iron, cadmium, aluminium, and magnesium. From the standpoint of cost, capacity, and convenience, zinc is the preferred material. Although the anode can be in the form of a solid or substantially solid metal sheet, it is preferred that the anode be porous. Porous anodes can be made, for example, by sintering select metal powders.

The cells will operate on conventional electrolytes including the alkali materials such as sodium hydroxide, and potassium hydroxide. Acid electrolytes including sulfuric acid, phosphoric acid, and hydrochloric acid can be employed. As is apparent, depending upon the particular electrolyte used, different anode materials can be selected. It is also feasible and at times desirable to employ an electrolyte which is trapped in a suitable matrix such as those made up of hydrophilic polymer or ceramic materials.

WHAT WE CLAIM IS:—

1. A metal/air battery comprising a plurality of cells each comprising a non-consumable air-depolarized cathode comprising a hydrophobic member and a conductive catalytic coating on one surface of said member, a consumable metal anode spaced from and opposite said catalytic coating on said cathode and an electrolyte in the space separating said cathode from said anode, spacers separating said plurality of cells from each other permitting air flow to said cathodes, and means constructed and arranged integral with said plurality of cells for propelling air across said air-depolarized cathodes.

2. A battery as claimed in claim 1, wherein said means for propelling air across said air-depolarized cathodes is an electric fan constructed and arranged to operate on a portion of the current output of said battery.

3. A battery as claimed in claim 1 or claim 2 including means for sensing the voltage of said plurality of cells when current is being drawn from said battery and (a) increasing or decreasing the number of said plurality of cells connected in a current producing circuit in response to a voltage change to maintain the battery within a fixed voltage range, and/or (b) controlling said means for propelling air to vary the air flow across said cathodes.

4. A battery as claimed in claim 3, wherein said means for propelling air and means for sensing the voltage are in series connection whereby said means for propelling air is only in operation when all of said plurality of cells are on load.

5. A battery as claimed in any of claims 1 to 4 wherein said consumable metal anode and the cathode have mated plug and socket terminals permitting replacement of the metal anode by disengaging the plug from the socket.

6. A battery as claimed in any of claims 1 to 5 wherein the battery includes a receptacle for retaining said plurality of cells and spacers, said receptacle having a plurality of openings for the passage of air, and a cover.

7. A battery as claimed in claim 6, wherein said cover includes a housing for said means for propelling air and said means for sensing the voltage of the plurality of cells.

8. A battery as claimed in any of claims 1 to 7 including a fixed end plate at one end of said plurality of cells and separated from the end cell of said plurality of cells by a spacer and a movable end plate at the other end of said plurality of cells constructed and arranged with a screw-drive mechanism for applying and releasing pressure on said plurality of cells.

9. A battery as claimed in any of claims 1 to 8 wherein the consumable metal anode is zinc.

10. A battery as claimed in any of claims 1 to 9 wherein the hydrophobic member of said cathode is polytetrafluoroethylene and said conductive catalytic coating on one surface of said member comprises a uniform mixture of catalyst and hydrophobic polymer particles.

11. A battery as claimed in claim 10, wherein the hydrophobic polymer is polytetrafluoroethylene.

12. A battery substantially as hereinbefore described with reference to and illustrated in the accompanying drawings.

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1221196 COMPLETE SPECIFICATION

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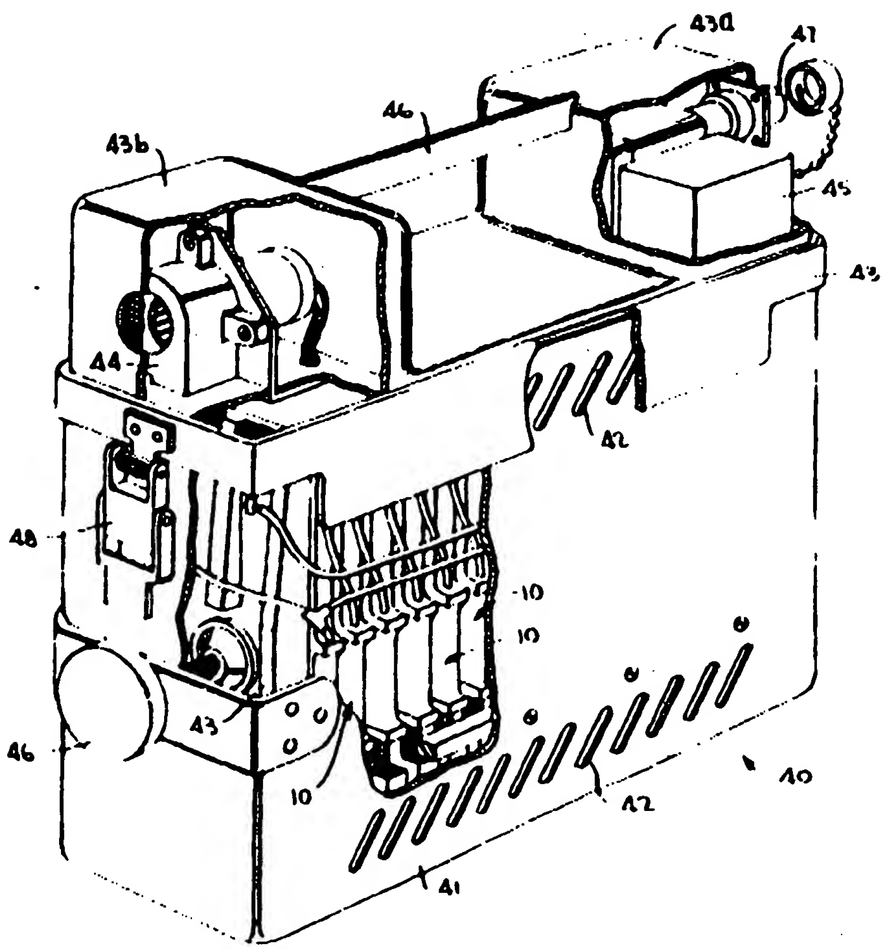
Sheet 1

FIG. 1



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Sheet 2

FIG. 2

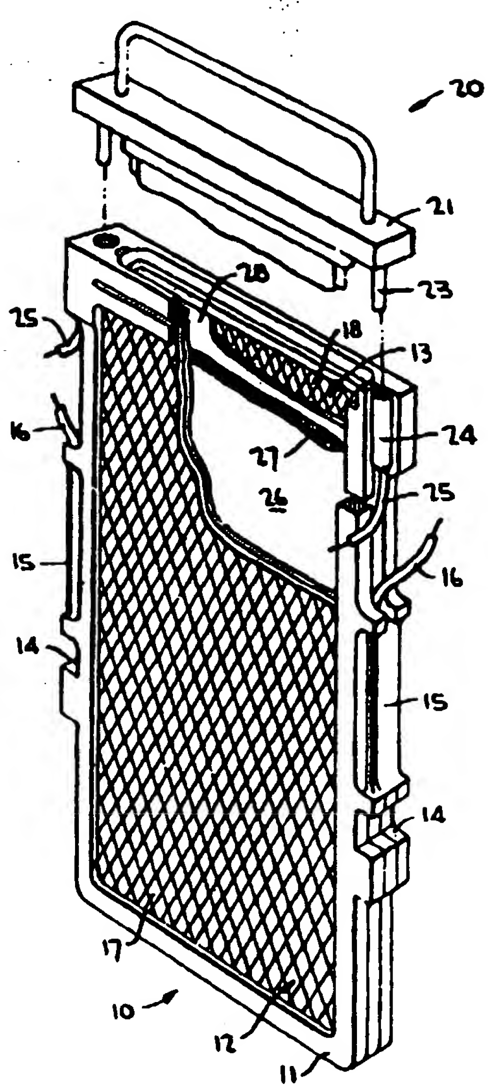

FIG. 3

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Sheet 3

FIG. 4